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BASIC AND APPLIED RESEARCH IN MATERIALS

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## I. SUMMARY

This report covers the period 1 June 1974 through 30 November 1974 and describes the research carried out in three major areas: 1) Materials for Energy Storage, 2) Heterogeneous Catalysis and 3) Maximization of Electret Effect in Polyacrylonitrile Films.

### A. Technical Problem and Approach

#### 1. Materials for Energy Storage

The discovery of new types of solid electrolytes (such as beta alumina,  $\text{RbAg}_4\text{I}_6$ , copper and silver halides and stabilized zirconia) with large values of ionic conductivity at relatively low temperatures has enhanced the prospect of developing battery systems possessing a high energy storage-to-weight ratio, high power output capability, long life in service, efficiency in charge-discharge characteristics and the capability of being constructed from inexpensive, readily obtainable materials. Three complementary areas of research are being pursued. The first involves a search for new materials to be used as solid state electrolytes and electrodes; the second involves detailed studies on electrolytes already known to be predominantly ionic conductors, and the third involves a fundamental investigation of sintering and hot pressing of materials of interest. Toward these ends, the studies begun the previous year on the cuprous halides as model systems are being completed. The search for electrolyte materials is being concentrated on the hollandites, which are capable of operating at ambient temperatures. Mössbauer and NMR techniques are being used to characterize these materials. Solid electrode materials under investigation include the tungsten and vanadium bronzes. The sintering studies are being pursued in order to develop methods of preparing dense, polycrystalline electrolytes and electrode materials.

#### 2. Maximization of Electret Effect in Polyacrylonitrile Films

Dielectric solids possessing a permanent electric field (electrets) can potentially be used as active elements in a number of devices, e.g., acoustical transducers, infrared detectors, piezoelectric devices and optical second harmonic generators. Polymeric solids make superior electrets

because of their thermal and mechanical stability, long chain macromolecular nature (which afford an additional means of orienting dipolar groups) and low cost. These properties will be exploited in the creation of new materials for use in apparatus utilizing the electret effect.

The purpose of the present research is to determine quantitatively the interrelations between molecular organization, electrical polarization and the coefficients of piezoelectricity and pyroelectricity in polyacrylonitrile (PAN) films and to establish active collaboration with staff members of the Instrumentation Application Section of the NBS. Current research is directed toward the direct measurement of polarization derivative quantities in PAN films utilizing various techniques, including x-ray scattering and birefringence measurements, the measurement of open-circuit potentials across poling electrodes, scanning electron microscope studies to attempt to observe the electrical polarization domains and thermally stimulated discharge currents.

### 3. Heterogeneous Catalysis

A number of the most important heterogeneous catalysts consist of tiny crystallites of metal supported upon a carrier such as silica or alumina. The support leads to a greater metallic surface area per gram of metal and permits use of the catalyst at temperatures up to 500°C without rapid sintering. However, relatively little is known of the exact nature of the crystallites (including the nature of their attachment to the support), the effect of the support upon the catalyst behavior, the effect of metallic particle size on catalytic characteristics and the effect of the method of catalyst preparation upon catalytic activity. It is the purpose of this project to provide some resolution of these problems.

Standard batches of catalysts are being prepared by different methods, of varying particle sizes and on different supports. These catalysts will be characterized as completely as possible using x-ray diffraction and scanning and transmission electron microscope studies (to determine crystallite size, orientation, strain, dislocation density and radial density function), EPR studies (to yield information about the migration of reactants and products on the support and, possibly, the nature of the catalytic sites on the metal),

kinetic studies (to determine the kinetic form and rate constants for reactions chosen to give optimum information about catalytic characteristics) and selectivity studies (to determine relative yields of several concurrent reactions). Analytical studies will be undertaken to correlate the data on the two sets of catalysts to be studied (on silica and alumina supports) in this project and to develop a theoretical understanding of the underlying phenomena.

## B. Technical Results

### 1. Materials for Energy Storage

Previously,  $\text{Ba}_x(\text{Ti}_{8-x}\text{Mg}_x)\text{O}_{16}$  [ $0.6 \leq x \leq 1.14$ ] compounds were produced by direct fusion of  $\text{BaO}$  and  $\text{TiO}_2$ , and polycrystalline hollandites were synthesized from high purity oxides and carbonates by a solid state reaction at  $1200^\circ\text{C}$ . Attempts are being made to prepare single crystals of the Ba hollandites using pressed and sintered rods of this phase as the starting material. Polycrystalline samples of some alkali titanates possessing the ramsdellite structure and of general formula  $\text{Li}_x\text{Ti}_{4-x/4}\text{O}_8$  ( $2 \leq x \leq 3$ ) were prepared from high purity alkali carbonates and  $\text{TiO}_2$  powders. Polycrystalline  $\text{Li}_2\text{Ti}_2\text{O}_8$  samples were also synthesized. NMR measurements on this and two compounds of the family  $\text{Li}_x\text{Ti}_{4-x/4}\text{O}_8$  are highly encouraging. Preliminary conductivity measurements on  $\text{Li}_{2.4}\text{Ti}_{3.4}\text{O}_8$  were also performed.

Total conductivity measurements are being performed on samples of sodium  $\beta''$ -alumina prepared previously. The total electrical conductivity of CuI was measured over the range  $75^\circ - 450^\circ\text{C}$ . Electron hole conductivity for the range  $255^\circ - 450^\circ\text{C}$  was also obtained.

The electrolyte,  $7\text{Bi}_2\text{O}_3 \cdot 2\text{WO}_3$ , was prepared by a novel method which permits synthesis at substantially lower temperatures than is possible with conventional powder preparation. A study was undertaken to determine the optimum calcining and sintering temperatures for this material.

A model has been developed for sintering retarded by a surface particulate dispersoid and is being readied for publication. A model is also being prepared which describes the ionic conduction in systems containing a bulk dispersoid.

The diffusivities of  $\text{Na}^+$  ions is being evaluated in some alkali hollandite phases previously prepared for use as electrodes. Single crystals of  $\text{Na}_x\text{WO}_3$  ( $0 \leq x \leq 1$ ) were also prepared, and the partial molar thermodynamic properties for Na in  $\text{Na}_x\text{WO}_3$  were determined.

## 2. Maximization of Electret Effect in Polyacrylonitrile Films

Using thermally stimulated discharge techniques, two major depolarization peaks have been isolated as the temperature of PAN (which had been strained prior to poling) was increased. Activation energies for the process associated with each of these peaks were obtained. Birefringence and x-ray scattering studies of electrically polarized PAN have shown that the dipolar nitrile side groups adopt an average orientation in the direction of the electrical field. Preliminary SEM experiments have revealed small-scale contrast effects whose shape is similar to that of magnetic polarization domain structures.

## 3. Heterogeneous Catalysis

The hydrogenolysis of cyclopropane experiments have been performed on several catalysts prepared during the first year and turnover numbers and activation energies obtained. Preliminary measurements were made on the adsorption of di-t-butyl nitroxide on silica gel; this will provide information about surface mobility on the support. The apparatus for the study of the isotopic exchange between cyclopentane and deuterium was placed into operation, and all of the catalysts have been examined at 80, 90, 100 and 110°C. X-ray measurements of the surface area of the silica gel support for our catalysts are now in progress. An additional study of the dispersion measurements has been completed; this study was motivated by the discrepancies between these measurements as performed by two industrial laboratories.



## II. RESEARCH REPORTS

### A. Materials for Energy Storage

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- J. B. Wagner, Professor, Materials Science
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This research is focused on promising solid materials for use in high performance, rechargeable battery systems to operate at ambient temperatures. The overall objective here is the investigation of solid-state electrolyte and electrode materials for use as power sources for both: (1) high-power, high energy-density secondary battery systems for vehicle propulsion; and (2) low-power, long-life applications such as in electronic equipment.

Specifically, this investigation is aimed towards developing: (1) a better understanding of the effects of structure and composition on transport mechanisms in solid electrolyte materials which exhibit fast ionic diffusion; (2) a detailed knowledge of the kinetics and mechanisms of reactions occurring (on a microscopic scale) at the cathode-electrolyte interface with a view towards eliminating polarization effects prevalent at operating temperature; (3) fabrication and joining techniques needed to combine solid electrodes

with solid electrolytes in various battery configurations; (4) new solid electrolytes and characterizing their properties; and (5) electrochemical techniques for the preparation, characterization and modification of properties of solid materials. Toward these ends, a variety of screening techniques to identify likely candidates as well as techniques to characterize materials of interest are being employed. Screening techniques include the methods of ion exchange, dielectric loss and nuclear magnetic resonance (NMR) line narrowing. Following the screening experiments, materials are characterized by measuring the rate of ionic transport in the successful solid electrolyte and electrode candidates. The techniques include the potentiostatic technique, direct conductivity studies and tracer diffusion studies.

During the first year, work was begun on new electrolyte materials based on rutile which possess the hollandite structure. Direct fusion of BaO and  $\text{TiO}_2$  in our laboratories produced a Ba hollandite phase which was invariably bluish-black in color and was a good electronic conductor due to the presence of Ti ions in two different valence states. The  $\text{Ba}_x(\text{Ti}_{8-x}\text{Mg}_x)\text{O}_{16}$  [ $0.6 \leq x \leq 1.14$ ] compounds produced in this manner possessed a channel structure formed by a host framework  $(\text{Ti}_{8-x}\text{Mg}_x)\text{O}_{16}$ , with the  $\text{Ba}^{2+}$  ions occupying some of the available lattice sites within the tunnels. Polycrystalline hollandites were also synthesized from high-purity oxides and carbonates by a solid state reaction at  $1200^\circ\text{C}$  as suggested by Singer et al. Attempts are now being made to prepare single crystals of the Ba hollandites using pressed and sintered rods of this phase as the starting material and a hollow cathode-plasma beam-floating zone method.

In a continuation of electrolyte synthesis work during the present contract year, polycrystalline samples of some alkali titanites possessing the ramsdellite structure were prepared from high-purity alkali carbonates and  $\text{TiO}_2$  powders. The powders were mixed in the proper proportions in acetone to yield the composition  $\text{Li}_x\text{Ti}_{4-x/4}\text{O}_8$  ( $2 \leq x \leq 3$ ), the mixture then being dried, compacted in a die and pre-sintered at  $800^\circ - 900^\circ\text{C}$  for several hours. The resulting compact was subsequently crushed and the powder repressed and sintered at  $1100^\circ\text{C}$  for about 3 days. The ramsdellite structure is related to the rutile structure except in the former the octahedra are



rearranged so that the tunnels in which the  $\text{Li}^+$  are accommodated are two ( $\text{TiO}_6$ ) octahedra wide.

Polycrystalline samples of  $\text{Li}_2\text{Ti}_2\text{O}_5$  were synthesized from carbonate and oxide powders in the manner described above for the ramsdellite phase. The  $\text{Li}_2\text{Ti}_2\text{O}_5$  compound crystallizes with tetragonal symmetry and is closely related to the tetragonal tungsten bronzes. It was also expected here that the  $\text{Li}^+$  ions would be mobile in the two types of channels which exist in the tetragonal bronze structure.

NMR line narrowing results between 77° and 300°K on the compound  $\text{Li}_2\text{Ti}_2\text{O}_5$  as well as two compounds from the family  $\text{Li}_x\text{Ti}_{4-x/4}\text{O}_8$  have been highly encouraging; the  $^7\text{Li}$  resonance fully narrows between 77° and 300°K, indicating that there is indeed rapid  $\text{Li}^+$  ion motion in these compounds. The data are summarized in the table below. Since the NMR technique cannot

Compound	Activation Energy (eV/ion)	Jump Frequency for $\text{Li}^+$ ( $\text{sec}^{-1}$ )
$\text{Li}_2\text{Ti}_{2.25}\text{O}_5$	0.15	$1.6 \times 10^8$
$\text{Li}_{2.4}\text{Ti}_{3.4}\text{O}_8$	1.11	$5.0 \times 10^7$
$\text{Li}_2\text{Ti}_2\text{O}_5$	0.11 (High T Process) 0.26 (Low T Process)	$2.4 \times 10^{10}$

readily differentiate between localized and long-range  $\text{Li}^+$  ion transport in these phases, it is necessary to use other techniques, such as the measurement of dc conductivity using reversible electrodes applied to the electrolyte sample, to ascertain whether the  $\text{Li}^+$  ion motion is really long-range. To date, preliminary conductivity measurements have been done on the compound  $\text{Li}_{2.4}\text{Ti}_{3.4}\text{O}_8$  using solid Li metal reversible electrodes; these results clearly indicate that the  $\text{Li}^+$  ion transport in this compound is of a long-range character and that the activation energy for conductivity is somewhat  $< 0.2$  eV/ion. It does appear, however, that the activation energy value for

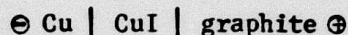
ionic conductivity, although low, is somewhat higher than that inferred from the NMR line-narrowing data (0.11 eV/ion). This discrepancy in activation energy values will be resolved, hopefully, by undertaking more extensive conductivity measurements and extending the temperature range for the measurements above the melting point of Ti (186°C) through the use of molten  $\text{LiNO}_3$  as the reversible electrodes. On the basis of the uncertainties in the data, the activation energies listed above are probably correct to within  $\pm 10\%$ .

The presence of the two distinct, temperature dependent processes in the  $\text{Li}_2\text{Ti}_2\text{O}_5$  is surprising; however, there are two different-sized tunnels in the structure. The observed line shapes do not particularly suggest the presence of a very narrow line superimposed on the relatively broad line which might be expected when two processes with different activation energies are present. This possibility will be re-examined. In all cases, the line shape, as expected, changed from Gaussian at low temperatures to Lorentzian at temperatures at which the line width was approximately half of its low-temperature value.

During the previous year, discs of sodium  $\beta''$ -alumina were prepared by mixing  $\text{Al}_2\text{O}_3$  powder with  $\text{Na}_2\text{CO}_3$  and small concentrations of  $\text{ZrO}_2$  and  $\text{MgO}$ , compacting and sintering this at 1000°C. The additives  $\text{ZrO}_2$  and  $\text{MgO}$  were found to improve the sinterability of the  $\beta''$ -alumina compact. The total conductivity measurements are now underway on such samples utilizing sodium tungsten bronze as the reversible electrode. Preliminary results indicate that a thin dielectric layer forms on the surfaces of the sodium  $\beta''$ -alumina sample which have been in contact with the tungsten bronze electrodes; this layer undoubtedly results from a reaction between the electrodes and the sample and undoubtedly gives rise to spurious conductivity results. Accordingly, other reversible electrode materials will be sought out.

In a continuation of research initiated last year, the total electrical conductivity of CuI has been measured in the temperature range of 75° to 450°C. An ac bridge was used with the CuI pellet pressed between reversible, copper electrodes. An Arrhenius plot of the data exhibits curvature for the low temperature gamma phase indicating that more than one type of defect participates in the conduction process. The higher temperature

(alpha and beta) phases exhibit fairly linear Arrhenius plots. These data are in good agreement with those of Bierman and Oel. An asymmetric polarization cell of the form



was used to obtain the electron hole conductivity of CuI in the temperature range of 255° to 450°C. The latest data follow the expected equation for the electronic current  $I$ , i.e.,

$$I = (ART/FL) \{ \sigma_e^0 [1 - \exp(-EF/RT)] + \sigma_h^0 [\exp(EF/RT) - 1] \}$$

where  $L$  is the length of the electrolyte,  $A$  is the area,  $\sigma_e^0$  and  $\sigma_h^0$  the partial conductivities of electrons and holes, respectively, of the electrolyte in equilibrium with the reversible electrode,  $E$  the applied potential difference,  $F$  the Faraday constant,  $R$  the gas constant and  $T$  the absolute temperature. CuI conducts electronically primarily via electron holes. Accordingly, plots of  $\log I_{\oplus}$  versus the bias voltage yield the theoretical slope,  $F/RT$ . The transport number for electron holes,  $t_{\oplus} \equiv \sigma_{\oplus}^0 / \sigma_{\text{total}}^0$ , is  $< 10^{-2}$  for the high temperature, alpha phase so that CuI may be useful as an electrolyte. By measuring the current-time curves in response to an abrupt change in bias voltage on the above cell, the diffusion coefficient and hence the mobility for the electron holes may be obtained. A new method is currently being developed to use these same data to obtain the mobility of the mobile ion. Basically, the transient response current is analyzed using the continuity equation for the ions including diffusion, drift and recombination terms. A drift mobility of  $\sim 1.5 \times 10^{-3} \text{ cm}^2/\text{sec}$  has been obtained for  $\text{Cu}^+$  in CuI at 450°C.

The material,  $7\text{Bi}_2\text{O}_3 \cdot 2\text{WO}_3$ , is a fast oxygen ion conductor--useful as an electrolyte at temperatures  $\gtrsim 600^\circ\text{C}$ ; thus it can be used at lower temperatures than calcia stabilized zirconia. During the first year, we synthesized this material by calcining bismuth nitrate, milling with tungstic acid, calcining the resultant mixture and then cold pressing to yield a compact of 67% theoretical density. However, we have now succeeded in preparing this material using a novel method originally developed to produce  $\text{BaTiO}_3$ . Bismuth nitrate was dissolved in a solution of citric acid in ethylene glycol. Tungstic acid, in the proper proportions, was then added, and the resulting mixture was heated while being stirred. The result was an organic glass



containing the bismuth salt in solution and the finely divided tungstic acid in suspension. This mixture was then calcined at  $\geq 650^{\circ}\text{C}$  to decompose the organic materials and burn off the excess carbon. The final product was a homogeneous compound prepared at substantially lower temperatures than those employed in more conventional powder preparation.

A systematic study was undertaken to determine the optimum calcining and sintering temperatures for this material. It was found that the optimum calcining procedure was 1 hour at  $675^{\circ}\text{C}$  and for sintering, 1 hour in air at  $950^{\circ}\text{C}$ . This resulted in compacts of approximately 92% of theoretical density. It was found that the sintering temperature is just below a peritectic temperature and that sintering was accomplished in the presence of a substantial amount of liquid phase. Additional research will be required to determine whether a longer sintering time at lower temperatures can achieve higher final densities. The grain size after firing was approximately  $20\text{ }\mu\text{m}$ ; grain growth apparently occurred early in the sintering process and was nearly independent of time beyond one hour. It was observed that the grain size was a function of calcining temperature, with a minimum grain size occurring at  $675^{\circ}\text{C}$ . Studies are being continued to understand this phenomenon.

Since many electrolyte materials will be prepared by sintering, it is important to gain an understanding of the various sintering mechanisms. There is considerable interest in devising means of retarding surface area loss through sintering. It has been known for a number of years that dispersed oxide particles cause a reduction in the rate of sintering of metals. A model for sintering retarded by a surface particulate dispersoid has been devised and is being prepared for publication. It is based upon the assumptions that mass transport in many cases occurs by surface diffusion, that the surface particles pin the surface but are mobile, and that the rate of motion of the particles is governed by the interfacial diffusion of the sintering material in the interface between the dispersed particle and the material. The model predicts that particles which are more nearly wet by the material will be more effective than non-wetted particles in retarding sintering. In addition, for a given volume fraction of dispersoid phase, larger dispersoid particles are more effective for sintering retardation. The most important factor for sintering retardation is the magnitude of the interfacial

diffusion coefficient compared with the surface diffusion coefficient. There are practically no data in the literature for interfacial diffusion between an oxide and a metal. Experimental verification and application of the model are being initiated.

One of the most interesting, and potentially useful, discoveries in the area of ionic conduction in solids was the observation by Liang that an alumina dispersoid in LiI caused more than an order of magnitude enhancement of the ionic conductivity. The implications of this discovery in battery technology are obvious. It remains to be seen to what extent this might be a general phenomenon.

Liang did not attempt to explain the phenomenon. A model is being prepared which describes the ionic conduction in systems containing a bulk dispersoid. It is apparent at this stage that Liang's results cannot be described in terms of enhanced conduction at the electrolyte-dispersoid interface. Although the model is not yet in final form, it appears that enhanced ionic conduction in a space charge layer surrounding the dispersoid particles will account for the observed effect. Further work on the model is under way.

Some alkali hollandite phases were prepared during the first year by the reduction of an alkali titanate at 1000°C for use as electrode materials. They exhibit the properties that make them excellent candidates for this purpose. We are still in the process of evaluating the diffusivity of  $\text{Na}^+$  ions in this material using NMR line-narrowing techniques. Single crystals of  $\text{Na}_x\text{WO}_3$  ( $0 \leq x \leq 1$ ) were also prepared by electrolysis and the partial molar thermodynamic properties for Na in  $\text{Na}_x\text{WO}_3$  bronzes determined employing the EMF method. The sodium activities were determined, using pyrex glass as the solid electrolyte. The partial entropy, enthalpy and free energy of Na in  $\text{Na}_x\text{WO}_3$  were then calculated from standard thermodynamic relationships. The partial molar free energy of Na in the bronze has been observed to be a linear function of temperature over the range 400° to 600°C; accordingly, the partial molar enthalpy and entropy of Na are independent of temperature over this range. Moreover, it has been found that these thermodynamic quantities become more negative as the sodium content of the bronze decreases.



## B. Maximization of Electret Effect in Polyacrylonitrile Films

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The objectives of this research are twofold:

1) over the long term, to develop fundamental information on relationships between molecular organization in polymer solids and those physical properties which are related to the permanent electrical polarization of these solids; and

2) over the short term, to characterize the origins of electrical polarization in polyacrylonitrile solids whose chains have been oriented to various amounts by uniaxial strain. Special emphasis will be given to developing an understanding of the 180°C peak seen in thermally stimulated discharge experiments because this peak is associated with electrical polarization which reforms spontaneously after being discharged; furthermore, this polarization can be reversed by poling in the opposite direction. This polarization "memory" and "switching" behavior are hitherto undiscovered properties of polyacrylonitrile electrets and, possibly, of polymer electrets in general. Unique electronic devices may conceivably be designed and constructed to exploit this unusual property.

Polymer solids possessing a permanent electrical polarization (electrets) are currently being utilized in a variety of new devices including microphones, temperature sensors, pressure transducers, strain gauges, radiation dosimeters and optical second-harmonic generators. The ferroelectric properties of these solids can also be exploited for devices utilizing electrical memory.

Polymeric films are excellent materials from which to make electrets because they are inexpensive and possess considerable variation in chemical composition, physical anisotropy, thermal stability, chemical inertness and

mechanical strength combined with flexibility. This research seeks to establish relationships between those key properties of polymer electrets that make them so useful for device applications and the basic physical or chemical microstructures that control electret performance characteristics.

Permanent electrical polarization in polymer solids has been studied at a number of laboratories on electrets of varying compositions and microstructures and with various origins of electrical charge. Results have shown that charged species may be introduced in surface layers by injection during corona discharge (in which case opposing surfaces may both have the same polarity) or during poling (in which case a homocharge gives opposing surfaces opposite polarity). Furthermore, if the dipolar moieties within the solid possess some net preferred orientation, then the specimen will exhibit a corresponding permanent electrical polarization. Space charges can also be asymmetrically distributed to create an additional contribution to net electrical polarization. Finally, adsorbed molecules can accumulate on the specimen surfaces and create a charged zone. Depending upon the relative magnitudes and polarities of the various charging effects, a sample will possess a net polarization that can vary in sign and in magnitude from zero to a very large value.

Relationships between microstructural and molecular organizational effects in polarized polymers are only now being investigated. Studies on polystyrene, poly(methyl methacrylate), poly(ethylene terephthalate), poly(vinyl alcohol), poly(tetrafluoroethylene), poly(vinylidene fluoride) etc. have shown that orientation of polymer chains can cause changes in the electret effect. In some cases this orientation is accompanied by the formation of crystals, in which case the polarization magnitudes are usually reduced; in certain cases where crystallization does not occur, the electrical polarization increases or decreases by small amounts, depending upon the polymer under study. It has been proposed that if polarization is due to oriented dipolar moieties in the chains, then the maximum polarization will be achieved by avoiding conditions which lead to development of order between chains (e.g., crystallization). Alternatively, if the polarization is a result of charged species located within the polymer bulk, then the

interfaces between crystalline and amorphous regions are desirable because they offer "stabilized" sites for the accumulation of such ions. How the derivatives of polarization with respect to temperature, pressure and strain are affected by different molecular organizations has not been studied; however, on the basis of work by Broadhurst and co-workers, there may well be a direct connection between polarization derivative quantities and the mechanical effects which result from the various microstructural states of these dipolar polymers. Finally, although the foregoing makes reference to many unknown structure-property relationships of importance to new materials technologies based on electrets, there is also the question of precisely what is the distribution of charge asymmetry due to each of the possible contributions to electrical polarization.

During the first year of this project, it was found that greater than a four-fold increase in polarization could be achieved in polyacrylonitrile—which ordinarily does not develop high levels of polarization as a result of standard poling treatments—if the material was strained beyond its natural draw ratio prior to poling. This increase is larger in polyacrylonitrile than in other electret-formers and may result from the disruption of clusters of nitrile side groups (possibly  $10^2$  per cluster) as the main chain backbones become uniaxially oriented. Using thermally stimulated discharge techniques (TSD), we have since isolated (following suitable "cleaning" procedures) two major peaks—the first with a maximum located at about 90°C (Fig. 1) and the second with a maximum located at about 180°C (Fig. 2). If the material is stretched, a slight decrease is observed in the 90°C peak, while a large increase occurs in the 180°C peak. Independently applying the theories of Chen and of Cowell and Woods, an activation energy for each depolarization process has been obtained; furthermore, it has been shown that the contribution to polarization represented by each peak is due to a charge asymmetry uniformly distributed across the film thickness direction. The 90°C peak corresponds rather well to the mechanically active transition known to exist in polyacrylonitrile; therefore, we conjecture that this peak results from randomization of nitrile side group orientations. However, the 180°C has no counterpart in the mechanical relaxation spectrum and is presumed, therefore, to originate from separated charges of some unknown character.

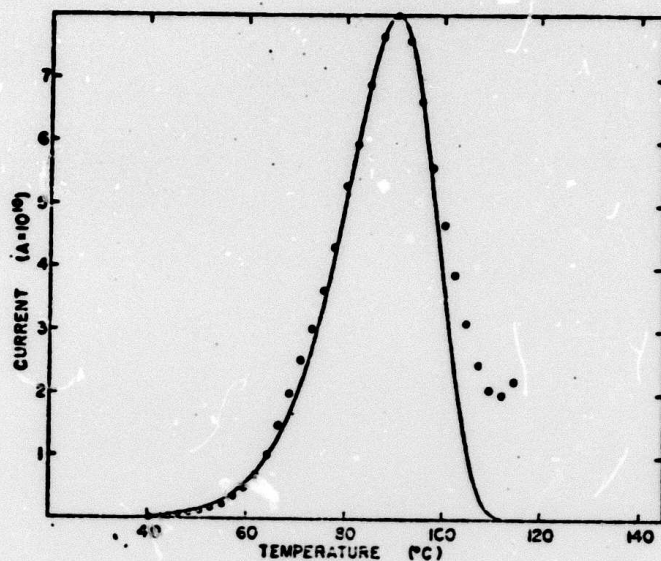


Figure 1. Cowell and Woods curve fit for a "cleaned" 90°C peak from an unoriented PAN film (Sample NSFII/g). (o = experimental data; — = theoretical curve with  $E = 27.7$  Kcal/mole).

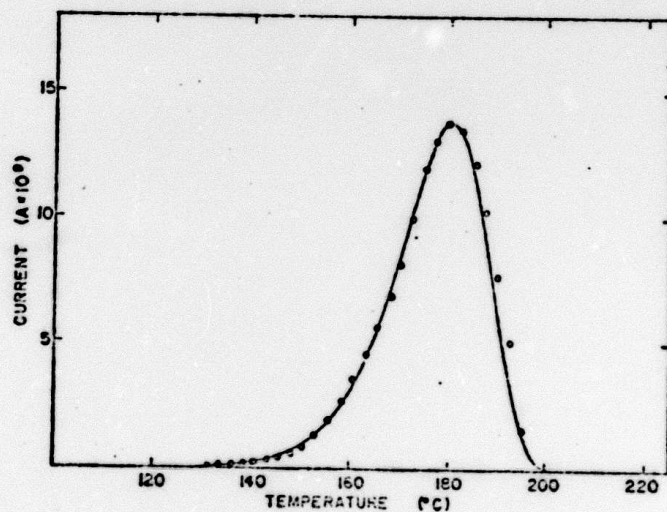


Figure 2. Cowell and Woods curve fit for 180°C peak for an unoriented PAN film (Sample NSFII/h). (o = experimental data; — = theoretical curve with  $E = 45$  Kcal/mole).



Computation of the maximum polarization that could result from perfect parallel orientation of nitrile groups yields a value that is an order of magnitude too low to account for the  $180^{\circ}\text{C}$  peak. Thus, this peak must be attributed to some type of space charge effect. Two additional features of interest regarding the  $180^{\circ}\text{C}$  peak are its ability to reform after the specimen has been cooled to room temperature and the fact that its polarity can be reversed by poling at a temperature  $50^{\circ}\text{C}$  below the maximum in its depolarization current. It is important to establish a better understanding of this peak because it might well be the basis for the ferro-electric-type memory and switching properties of polyacrylonitrile.

Studies on the birefringence and x-ray scattering properties of electrically polarized polyacrylonitrile have revealed that dipolar nitrile side groups adopt an average orientation in the direction of the electrical field, but there is no appreciable change in the x-ray scattering pattern. These birefringence data strongly suggest that the electrical polarization actually originates, at least in part, from a preferred arrangement of dipoles. However, the fact that the x-ray scattering from polarized polyacrylonitrile (Fig. 3) appears to be virtually the same (curve c) as that

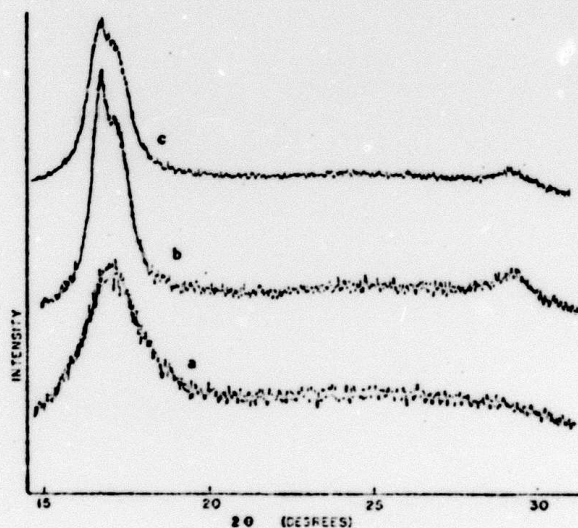


Figure 3. X-ray diffractometer scans (shifted arbitrarily to display on same axes) polyacrylonitrile in: a) its as-cast state, b) its annealed state (as necessarily results during a poling experiment), and c) its permanently polarized state.



obtained from materials heated once to the same temperature (curve b) suggests that bulk-average intermolecular organization has, in fact, not changed as a result of the electrical polarization. This observation is difficult to interpret unless one assumes that domains of the type which exist in classical ferroelectrics are also present in polarized polyacrylonitrile. In view of the preceding findings, one must also conjecture that stretching, which enhances the strength of the 180°C depolarization peak, either affects the origin of the space charge displacement mechanism or changes the domain structure of these electrets. Measurements of x-ray scattering from stretched and from stretched then polarized polyacrylonitrile reveal only subtle (but possibly significant) differences, as seen in Fig. 4. There, the slight doublet nature of the main scattering maximum diminishes in magnitude for films stretched and then polarized. The reasons for this are unclear but

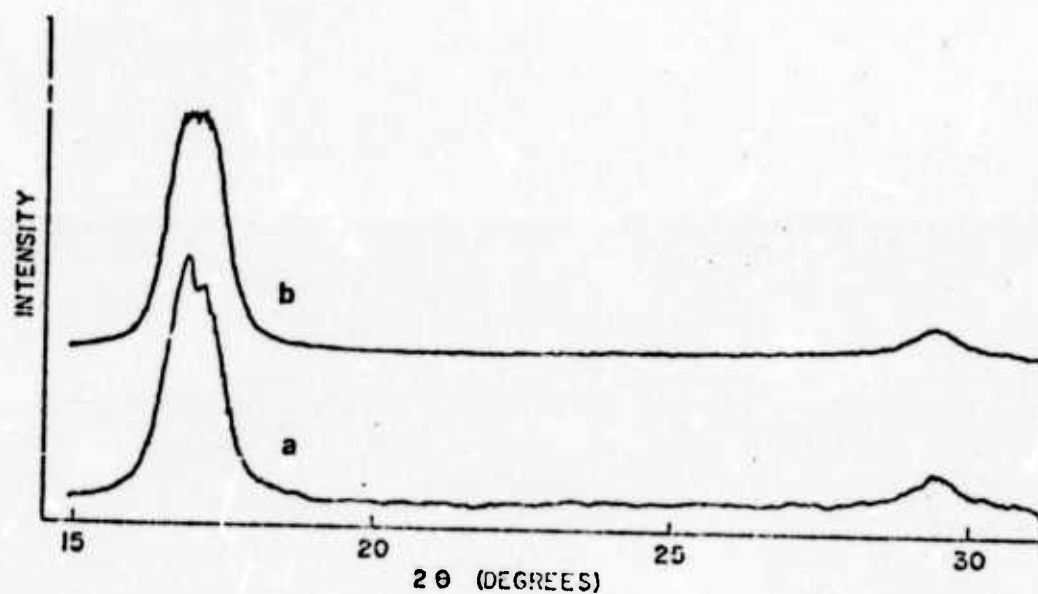


Figure 4. X-ray diffractometer scans from: a) stretched and annealed and b) stretched and then polarized polyacrylonitrile.

may be related to changes in texturization or to actual changes in intermolecular organizations. The former explanation would be correct if polarization domains existed, but the latter explanation would be more appropriate if extensive reorientation of dipoles was the result of poling.

Preliminary experiments on electrically polarized PAN with the scanning electron microscope (SEM) have revealed small-scale ( $\sim 1$  micron) contrast effects whose shape is similar to that of magnetic polarization domain structures. These details are apparently not associated with any surface topological features; thus, the implication is that these contrast effects arise from the bulk phase interaction between the scanning electron beam and the local polarization state. Two details in the sample preparation are significant here, i.e., the samples were uniaxially stretched prior to poling, and they contained an appreciable amount of sorbed iodine. There are a number of possible explanations to this observation; for example, stretching would force the dipolar side group to depart from participation in randomly configured clusters and to adopt an arrangement minimizing both strain energy in chains as well as energy due to the existence of local electrostatic fields. Conceivably, the relatively electron-dense iodine molecules simply enhance the magnitude of any possible electron beam-specimen interactions.

### C. Heterogeneous Catalysis

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This project is a collaborative study of supported metallic catalysts. Metallic catalysts of Group VIII such as platinum, palladium and nickel are of major importance both scientifically and technologically. A number of the most important catalysts consist of tiny particles of metal supported upon a carrier such as silica or alumina. The support leads to a greater metallic surface area per gram of metal since crystallite sizes on the support can be in the range of 15 - 150 Å. Furthermore, the presence of the support permits the catalyst to be used at temperatures up to 500°C without rapid sintering and the subsequent loss of metallic area. Although much is known about supported catalysts, relatively little is known either descriptively or theoretically of the following:

- 1) The exact nature of the crystallites, i.e., size, shape and nature of the attachment to the support;
- 2) The effect of the support upon the detailed catalytic characteristics of the metal;
- 3) The effect of metallic particle size and shape upon the catalytic characteristics; and
- 4) The effect of the method of catalyst preparation upon the details of catalytic activity.

It is the purpose of the present project to provide some resolution of these problems since supported catalysts are essential to the production of products in the petroleum and chemical industries worth tens of billions of dollars annually; ultimately, this affects all aspects of governmental and non-governmental activity. In particular, heterogeneous catalysis is closely involved in most aspects of energy consumption, and improvements in heterogeneous catalysis offer prospects of substantial reductions in the consumption of fuel. Toward these ends, the project was initially broken into the following segments:

- 1) Preparation of standard batches of catalysts for use of the entire group. These catalysts will be prepared by different methods, of varying particle sizes and on various supports.
- 2) Characterization by various physical methods including measurement of dispersion (the ratio of surface atoms of platinum to the total number of atoms of platinum expressed in percent), electron paramagnetic resonance

studies (to yield information about the migration of reactants and products on the support and, possibly, about the nature of the catalytic sites on the metal), x-ray diffraction and scanning and transmission electron microscopy studies (to determine crystallite size, orientation, strain, dislocation density and radial density function) and infrared spectroscopy of adsorbed molecules, e.g., carbon monoxide and nitric oxide (to provide further information concerning the nature of the catalytic site).

3) Evaluation by the investigation of several heterogeneous catalytic reactions upon the various catalysts. These reactions should include some that are independent of catalyst dispersion (hydrogenolysis of cyclopropane) as well as those which exhibit the maximum possible variation with dispersion (isotopic exchange distribution of cyclopentane). These studies include kinetic and selectivity studies.

4) Correlation of and a phenomenological explanation of the data followed by the development of a theoretical understanding of the underlying physical phenomena.

Platinum catalysts were chosen for the initiation of this project because there is more background information available for them than for the other metals, they are less easily poisoned and the procedure for the measurement of dispersion (percentage of surface atoms of the metal crystallites) appeared to be better defined. Silica was then chosen as the first support material to be studied primarily because it is the most inert of the materials commonly used as catalyst supports.

During the first year of this project, a set of eight Pt/SiO<sub>2</sub> catalysts were prepared. Davison wide-pore silica gel grade 62 was sieved and then treated with dilute nitric acid, washed and dried. Batches of Pt/SiO<sub>2</sub> were prepared by two different methods and a portion of each batch sintered. In addition, catalysts were duplicated--one set on 70-80 mesh silica gel and the other on 120-140 mesh. Much of the apparatus for characterizing the catalysts was constructed and preliminary measurements made.

During the present year, the hydrogenolysis of cyclopropane experiments were performed on several catalysts. Prior to making these later measurements, considerable effort was expended to establish procedures which



would yield reliable results. Experimental conditions were varied from  $-12^{\circ}\text{C}$  to  $22^{\circ}\text{C}$  at approximately one atm. total pressure and a hydrogen to hydrocarbon ratio of 15 to 1. At  $0^{\circ}\text{C}$ , the turnover number (number of reactions per catalytic site per unit time) obtained for catalyst 66 (impregnated with  $\text{H}_2\text{PtCl}_6$  aq, unsintered and 120 - 140 mesh size) was 0.116 at  $0^{\circ}\text{C}$  under the aforementioned conditions, while the turnover number for catalyst 70 (ion exchanged, sintered, 120 - 140 mesh size) was 0.190. A turnover number of 0.071 was obtained by Boudart and Dougharty for a similar catalyst. However, the pretreatment conditions of the catalysts were slightly different and the dispersion of Boudart's and our catalysts were different. Figure 5 shows the temperature dependence of the initial rate for catalyst 70. Both catalysts gave an activation energy of 8.4 kcal/mole, the same value as that reported by Dougharty and Boudart. It was expected that cyclopropane hydrogenolysis would be a structure insensitive reaction, i.e., that the rate of the reaction would depend only upon the number of exposed platinum atoms and not upon the dispersion or other structural features of the platinum crystallites. The data obtained thus far do not resolve this question, and further experiments are being carried out to settle this.

Further work was also performed on characterizing the surface mobility on the support. Catalysts containing the same metal but which are deposited on different supports may behave differently due to the electronic effects of the support upon the metal or to the surface properties of the support. For example, a reactant might exhibit different mobilities on different supports, an effect which would be important if the reactant adsorbed onto the support and migrated to the metal crystallite. Very little is known concerning relative mobilities of this type. However, we have developed a method which provides information on this subject. Di-*t*-butylnitroxide ( $((\text{t-bu})_2\text{NO})$ ) adsorbs very strongly on silica gel, and at room temperatures, the equilibrium pressure at low coverages is very small. We have adsorbed this air stable, free radical on  $\text{Pt/SiO}_2$  as well as on  $\text{Pt/Al}_2\text{O}_3$  and exposed the products to hydrogen. At room temperature, the free radical is very rapidly hydrogenated to di-*t*-butylhydroxylamine ( $((\text{t-Bu})_2\text{NOH})$ ). At  $-78^{\circ}\text{C}$ , the hydrogenation has a half-life of about 7 minutes when it is carried out on  $\text{Pt/SiO}_2$ . However, the same reaction is readily followed by electron



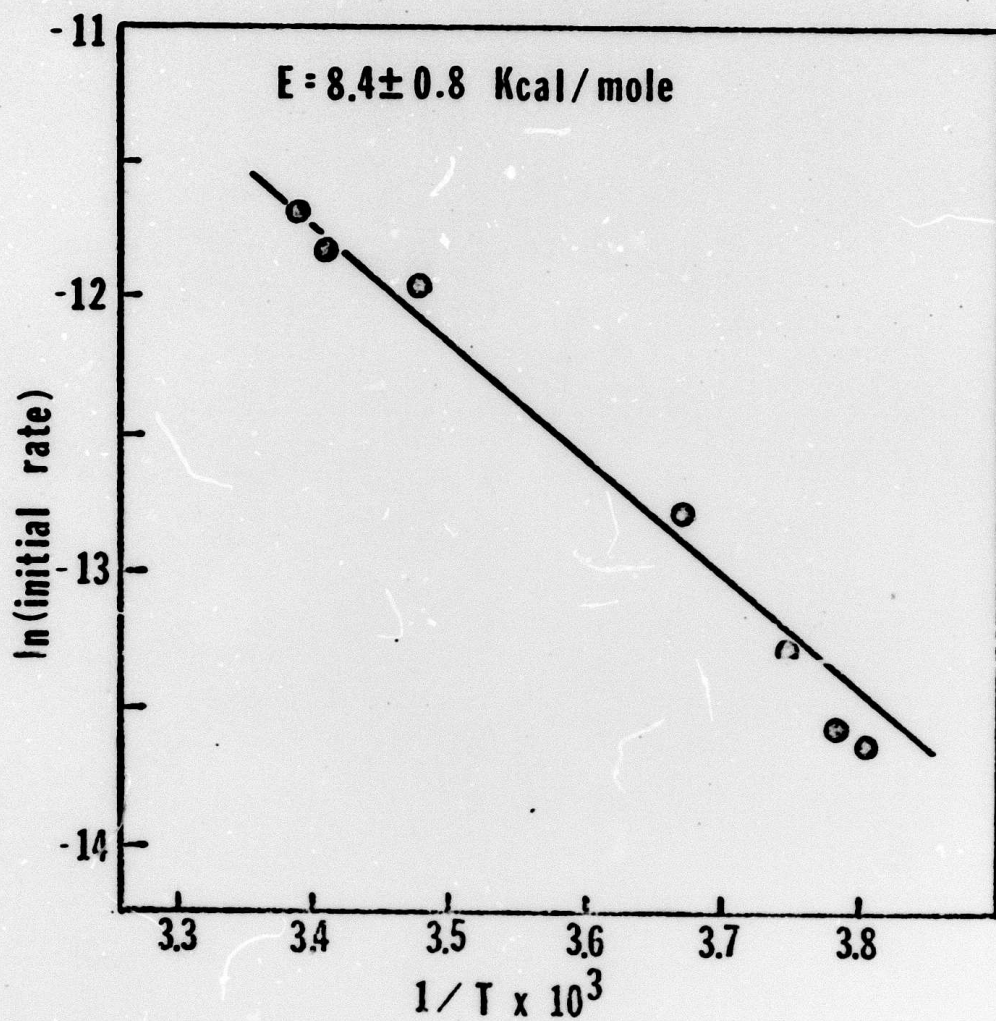


Figure 5. The dependence of the rate of hydrogenolysis of cyclopropane upon the temperature.

paramagnetic resonance. The shape of the signal provides additional details about the surface concentrations of the nitroxide and the nature of its attachment to the surface. Since the nitroxide is almost uniformly adsorbed on the silica (or alumina) and since the crystallites of platinum are widely separated, we believe that we are directly observing the migration of a reactant (the nitroxide) to the platinum crystallites. These preliminary measurements were not made on our standard catalysts; at a later stage in this project when both Pt/SiO<sub>2</sub> and Pt/Al<sub>2</sub>O<sub>3</sub> catalysts have been characterized and investigated, our standard catalysts will also be studied by this technique.

The apparatus for the study of the isotopic exchange between cyclopentane and deuterium was placed into operation. In this aspect of the project, cyclopentane vapor in deuterium is passed over a catalyst, and the cyclopentane is examined by mass spectrometry to determine the isotopic distribution, i.e., the percentage of the species C<sub>5</sub>H<sub>10</sub>, C<sub>5</sub>H<sub>9</sub>D, C<sub>5</sub>H<sub>8</sub>D<sub>2</sub> etc. (to be called D<sub>0</sub>, D<sub>1</sub>, D<sub>2</sub> etc.). Preliminary experiments indicated that the maximum differences in the isotopic distribution patterns between catalysts would be observed at temperatures near 90°C. All of the catalysts have been examined at 80°, 90°, 100° and 110°C. Some further work will be necessary to complete these data and to provide additional information on the exchange reaction. However, one can conclude that the reaction is distinctly structure sensitive, i.e., that it varies with dispersion. In particular, the ratio D<sub>10</sub>/D<sub>5</sub> for catalyst 88 (impregnated, sintered, 120 - 140 mesh) is only about 1/5th that of catalyst 66 (impregnated, unsintered, 120 - 140 mesh). Furthermore, the pretreatment conditions affect the distribution patterns although this effect is smaller than that due to the dispersion of the metal.

As reported last year, the small-angle equipment for the x-ray measurement of surface area has been completed, and a computer control program has been written and tested. This program calculates the surface area, radius of gyration and particle size distribution. Tests of the system on activated charcoal are complete, and good agreement with gas adsorption methods was obtained. Measurements on the silica gel support for our catalysts are now in progress and should be completed shortly.

Since the value of the dispersion is a particularly important criterion in characterizing catalysts, two industrial research laboratories were persuaded to determine dispersions of our catalysts using their techniques. The set of measurements carried out by the first industrial laboratory yielded almost the same ordering of dispersions as was obtained at Northwestern, but there were substantial discrepancies. The second set also produced discrepancies, but the two industrial sets did not agree between themselves. These discrepancies have forced us to undertake an additional study of the dispersion measurements which was not originally planned. The results indicate that trace impurities in the gases have very serious effects; our conclusion is that the values of the dispersions given previously are nearly correct although minor changes may be made as the research progresses. These will not affect the overall conclusions reached thus far.

There is evidence in the literature that the frequency of the infrared absorption bands of carbon monoxide adsorbed on platinum are structure sensitive. Data on the spectra of adsorbed carbon monoxide for our catalysts is thus potentially useful for overall correlations. The Union Carbide Research Laboratory, which has expertise in this area, has agreed to perform these experiments for this project. Samples of our  $\text{Pt/SiO}_2$  catalysts were, therefore, recently sent to them.

Following the completion of the studies on  $\text{Pt/SiO}_2$ , similar experiments are planned for  $\text{Pt/Al}_2\text{O}_3$ . Again, the catalysts will be prepared by two methods, in both sintered and unsintered form and of two mesh sizes. Since the preparation of these catalysts is extremely time consuming, we are fortunate that an industrial laboratory skilled in the art of catalyst manufacture has agreed to make them to our specifications. It is anticipated that this work will soon be underway and that preliminary experiments on these catalysts will commence soon thereafter.